

# Theoretical study of $C_{60}$ as catalyst for dehydrogenation in $LiBH_4$

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**Abstract.** Complex light metal hydrides possess many properties which make them attractive as a storage medium for hydrogen, but typically, catalysts are required to lower the hydrogen desorption temperature and to facilitate hydrogen uptake in the form of a reversible reaction. The overwhelming focus in the search for catalysing agents has been on compounds containing titanium, but the precise mechanism of their actions remains somewhat obscure. A recent experiment has now shown that fullerenes ( $C_{60}$ ) can also act as catalyst for both hydrogen uptake and release in lithium borohydride ( $LiBH_4$ ). In an effort to understand the involved mechanism, we have employed density functional theory to carry out a detailed study of the interaction between this complex metal hydride and the carbon nanomaterial. Considering a stepwise reduction of the hydrogen content in  $LiBH_4$ , we find that the presence of  $C_{60}$  can lead to a substantial reduction of the involved H-removal energies. This effect is explained as a consequence of the interaction between the  $BH_x^-$  complex and the  $C_{60}$  entity.

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## 1. Introduction

Hydrogen possesses many features which make it a highly attractive option as a future energy carrier [1, 2, 3, 4]. While such a transition is certainly not going to be easy, it is nonetheless inevitable to explore feasible alternatives to our fossil fuel resources which are finite and might even become exhausted within this century, and which furthermore involve carbon dioxide emissions linked to a harmful global climate change. Before one could even begin to realize such an envisioned hydrogen economy, a number of formidable technological problems need to be solved first. One of these issues is hydrogen storage [1, 2, 3, 4]. Pressurized gas tanks and cryostatic storage of hydrogen as a liquid do not seem ideal for mobile (vehicular) applications. Rather, storage of hydrogen inside solid materials appears to be the most feasible solution.

In this context, complex light metal hydrides are very promising as a suitable hydrogen storage medium. On the plus side, the gravimetric hydrogen content in these materials can be quite large, but a significant drawback is the generally high temperature required for hydrogen desorption and the fact that the reactions are often not reversible, i.e., hydrogen can be released, but the direct rehydrogenation is difficult or even impossible. To address this issue, catalysts are commonly added to the metal hydride systems, and particularly titanium has been shown to lower hydrogen desorption temperatures and enable reversibility [5], albeit the precise mechanism remains a topic of debate (for a discussion, see Refs. [6, 7]).

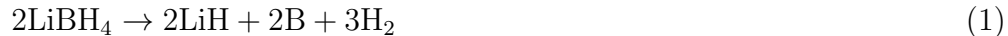
Studies of transition metal-catalysed hydrogen storage properties of sodium alanate (NaAlH<sub>4</sub>) went beyond Ti, and also considered Sc, Zr, and other early transition metals [8, 9, 10, 11, 12, 13]. Still, a fundamental understanding of how these catalysts, and in particular Ti, function has not been achieved yet [14, 15, 16, 17]. It is widely believed that a better insight into how a catalyst works could facilitate the rational design of novel catalysts for alanates, borohydrides, and amides.

Carbon nanomaterials have recently been added to the list of materials that could potentially act as “true catalysts” in the sense that they retain their structure and are not consumed in the reaction, and furthermore would be conceptually much simpler to understand in their action [18, 19, 20, 21, 22, 23]. Besides this function as catalysts [24, 25, 26, 27, 28, 29, 30, 31], carbon nanomaterials have also been considered for their role in nanoconfinement [27, 32, 33, 34, 35, 36, 37, 38] to aid in the hydrogen desorption process.

Previously, we presented the results of our study combining experiment and theory to demonstrate and understand the catalytic effects of various carbon nanomaterials on the hydrogen release and uptake in NaAlH<sub>4</sub> [23]. We found that the electron affinity of the studied carbon nanomaterials is mainly determined by the surface curvature and directly affects the hydrogen sorption mechanism of NaAlH<sub>4</sub>. One mechanism identified by us considers the higher electron affinity causing Na to donate more of its electronic charge to the carbon substrate, thus destabilizing the AlH<sub>4</sub> complex, which ultimately leads to a reduction in the H-removal energy. More recently, the experimental studies

were expanded to also cover hydrogen sorption in LiBH<sub>4</sub>, for which it was found again that carbon nanomaterials, and in particular fullerenes (C<sub>60</sub>), are excellent in their function as a catalyst [39].

Hydrogen desorption from LiBH<sub>4</sub> takes place in two steps:



Step 1 occurs above 400°C and releases 13.8 wt% hydrogen, while step 2 releases 18.4 wt% hydrogen and takes place at about 950°C which is too high a temperature to be considered practical (see Ref. [39] and references therein).

Here, we present the results from our first-principles analysis of the catalysing mechanism that enables C<sub>60</sub> to enhance the hydrogen desorption from LiBH<sub>4</sub>. In our previous work on NaAlH<sub>4</sub>, we had only considered the removal of a single hydrogen atom [23], but in the present study, we went further and explored the stepwise removal of up to three hydrogen atoms from LiBH<sub>4</sub>. This approach has led us to identify some new features in the C<sub>60</sub>-catalysed desorption reactions of LiBH<sub>4</sub> as compared to NaAlH<sub>4</sub>.

## 2. Computational methods

Total energy calculations were carried out within the framework of the generalized gradient approximation (GGA) [40] to density functional theory [41, 42] by using the projector augmented wave (PAW) method [43] as implemented in the Vienna Ab initio Simulation Package (VASP) [44]. PAW potentials with the valence states 1s for H, 2s for Li, 2s2p for B, and 2s2p for C were employed. The calculations under periodic-boundary conditions utilized a cubic supercell box with a side length of 20 Å, which prevented any unphysical interaction between repeated images and allowed us to consider only the  $\Gamma$ -point for Brillouin zone sampling. Atomic positions were relaxed with respect to minimum forces using a conjugate-gradient algorithm. To ensure that we identify indeed the ground-state structure, we initiated the relaxation process from several different starting configurations which saw the LiBH<sub>x</sub> unit (for  $x = 4, 3, 2$ , and 1) located at various potential trapping sites on the fullerene surface (such as on top of a C atom, on a C–C bridge, or a hollow site) and in various orientations.

## 3. Results and discussion

### BH<sub>4-x</sub><sup>0/-</sup>

Before introducing C<sub>60</sub>, we calculated the energetics for isolated BH<sub>4-x</sub> units ( $x = 0, 1, 2$ , and 3), both in the charge-neutral state (BH<sub>4-x</sub><sup>0</sup>) and with one extra electron added (BH<sub>4-x</sub><sup>-</sup>), and for the corresponding isolated LiBH<sub>x</sub> units. From this data, we calculated the gain in energy when a hydrogen atom is added and compared the results within each of these three systems, i.e., charged and neutral BH<sub>4-x</sub> and LiBH<sub>x</sub>. The findings from this analysis are summarized in figure 1. Quite analogous to our earlier

published analysis for AlH<sub>4-x</sub><sup>0/-</sup> [23], it is seen that the largest stabilization due to the extra electron occurs for the complex containing four hydrogen atoms, i.e., BH<sub>4</sub>.

We now turn to the main part of our investigation, namely the stepwise dehydrogenation in LiBH<sub>4</sub> when supported on C<sub>60</sub>. In the following, we present and discuss the results from our density functional calculations for each of the LiBH<sub>4-x</sub>+C<sub>60</sub> entities where  $x$  takes on the values 0, 1, 2, and 3.

### LiBH<sub>4</sub>

The most stable configuration has Li of the LiBH<sub>4</sub> unit centered above a C–C bridge (figure 2a). Other configurations which had LiBH<sub>4</sub> located at different sites on C<sub>60</sub> were tested, but were found to yield higher energies. For example, a 90°-rotation of the LiBH<sub>4</sub> unit (so that both Li and B would have roughly comparable distances to the fullerene surface) results in a drastic increase in energy by nearly 1 eV. Also, placing the LiBH<sub>4</sub> unit directly above the center of the hexagon yields a state about 0.25 eV higher in energy. The binding energy of LiBH<sub>4</sub> to C<sub>60</sub> is calculated as 0.50 eV, implying that the interaction is rather weak. A Bader analysis of the charge density shows that lithium has completely lost its electron. But this charge does not appear to have been transferred to the fullerene; rather, LiBH<sub>4</sub> as a whole is charge-neutral, so here the electron seems to have been used to stabilize the BH<sub>4</sub><sup>-</sup> unit, in line with what one would expect based on the results from our analysis of the energetics of the charged and neutral BH<sub>x</sub> units above. In addition, partial density of states (PDOS) calculations show that the B–H bonds in the BH<sub>4</sub><sup>-</sup> unit are of covalent nature, while the interaction between Li<sup>+</sup> and BH<sub>4</sub><sup>-</sup> is of ionic nature.

### LiBH<sub>3</sub>

Upon removal of the first hydrogen atom, we arrive at LiBH<sub>3</sub> supported on C<sub>60</sub>. Remarkably here, a configuration of the LiBH<sub>3</sub> unit similar to the upright one for LiBH<sub>4</sub> is not the most stable configuration. Instead, a “sideways” orientation (figure 2b) yields the ground state (0.86 eV lower in energy than the “upright” orientation). This enables the boron of the BH<sub>3</sub> unit to interact with one carbon atom of the fullerene, thus allowing it to preserve an approximate tetrahedral structure in the form of BH<sub>3</sub>C. One can even notice that the carbon atom has been slightly “pulled out” by the boron, distorting the hexagon somewhat. Indeed, PDOS calculations show that a bond of covalent nature is formed between B and this particular C atom. In a sense, this interaction of BH<sub>3</sub> with C<sub>60</sub> compensates for the loss of a hydrogen and substantially lowers the energy, as can also be seen from the greatly enhanced binding energy of LiBH<sub>3</sub> on C<sub>60</sub> (2.09 eV), and this plays a crucial role for the low H-removal energy of 2.82 eV in the first step (figure 3). However, it should be noted that the actual energy cost for removing the hydrogen atom is higher than that, due to a reaction barrier which was calculated by us with the nudged elastic band method [45] to be 4.3 eV high. As for the charge state, it is seen that lithium retains about 10% of its electron, but the LiBH<sub>3</sub> unit as a whole is missing −0.7 e, so here a substantial charge transfer to the C<sub>60</sub> has indeed taken place. In fact, the carbon atom closest to boron carries an excess −0.37 e. The rest of the charge is distributed over the other 59 carbon atoms of the fullerene. Thus, a complex

cooperative process is at work here, in which the extra electron that stabilized the BH<sub>4</sub> unit is no longer needed in BH<sub>3</sub> following the H atom removal, and can now instead facilitate the formation of a bond between B and C.

### LiBH<sub>2</sub>

Removal of the second hydrogen atom leads to LiBH<sub>2</sub> which just like LiBH<sub>3</sub> prefers a “sideways” orientation that is found to be more stable than the “upright” orientation (figure 2c). The difference in energy between these two possible configurations amounts in this case even to 3.5 eV, apparently owing to the now possible stronger interaction of boron with two carbon atoms of the fullerene. The binding energy of LiBH<sub>2</sub> to C<sub>60</sub> is 4.40 eV, about twice as much as in the case for LiBH<sub>3</sub>, reflecting that B interacts with two C atoms now. This is also seen from the PDOS, showing the formation of two covalent bonds between B and the two C atoms. The tetrahedral structure is again approximately preserved in the BH<sub>2</sub>C<sub>2</sub> configuration that is formed. Thus the two carbon atoms act again as substitutes for the removed hydrogen atoms and are seen to be “pulled up”, away from the C<sub>60</sub>, towards the boron, without actually breaking the C<sub>60</sub> framework. The lowering of the total energy through this form of interaction between BH<sub>2</sub> and the fullerene is once again responsible for the even further lowered H-removal energy of 2.38 eV in the second step (figure 3). The charge state situation is somewhat similar to the previous case of LiBH<sub>3</sub>, in the sense that lithium is charged positively with +0.88 e, but the LiBH<sub>2</sub> now carries an even higher positive charge of +1.4 e, twice as much as in the previous case. Of course, here, boron is interacting with two carbon atoms and indeed it is seen that they both receive about −0.5 e in excess charge.

### LiBH

After the third hydrogen atom has been removed, it is no longer possible for boron to easily preserve the preferred tetrahedral arrangement of binding partners as seen in the previous three cases. Instead, the BH unit continues to interact with two carbon atoms and only to a weaker extent with lithium (figure 2d). As a consequence, the H-removal energy in the third step is found to be not lowered, but quite oppositely, increased with respect to the situation of an isolated LiBH unit where no C<sub>60</sub> is present (figure 3). The binding energy of LiBH to C<sub>60</sub> amounts to 3.66 eV, similar to the value for LiBH<sub>2</sub>, due to both having B effectively interact with two C atoms, but reduced perhaps because of the strained non-tetrahedral configuration in which B finds itself. The PDOS again shows the formation of two covalent bonds between B and the two C atoms. We also tested the possibility of H attaching to Li rather than B, but the relaxation results indicate that H does indeed prefer to bind to B in this cluster.

## 4. Concluding remarks

Carbon nanomaterials certainly show great promise as catalysts for hydrogen sorption in complex light metal hydrides. In the present theoretical study, we have concentrated on the fullerene C<sub>60</sub> acting on the borohydride LiBH<sub>4</sub>, motivated by definitive experimental

evidence for the catalysing effects in this particular combination [39]. But as we had shown earlier [23], a similar outcome was seen for the alanate NaAlH<sub>4</sub>, and the carbonaceous catalysing agent was found to be not limited to C<sub>60</sub>, but could for example as well be high-curvature single-walled carbon nanotubes. Electron affinity certainly plays an important role, but not necessarily always the same role. For NaAlH<sub>4</sub> on various carbon substrates, we had found a charge transfer which presumably destabilized the AlH<sub>4</sub> complex [23]. Contrary to that, we did not find any theoretical evidence in our calculations here for charge transfer occurring from LiBH<sub>4</sub> to C<sub>60</sub>. Instead, the mechanism, which led to a sizeable reduction in the energy required to remove the first hydrogen atom in LiBH<sub>4</sub> relies on an increased stabilization of the product state, namely by formation of a “substitutional” bond between the B atom of LiBH<sub>3</sub> and a C atom of C<sub>60</sub>. That bond is however facilitated by a charge transfer reaction; hence electron affinity comes into the equation again. An analogous mechanism, now involving two C atoms, is responsible for the even further reduced hydrogen removal energy when going from LiBH<sub>3</sub> to LiBH<sub>2</sub>. Those are the main findings of this theoretical investigation.

Obviously, there are ways in which the present study could be improved. For example, our cluster approach only considered a single LiBH<sub>4</sub> unit interacting with C<sub>60</sub>. Although often, such minimal clusters mirror many of the important qualitative properties of the parent solid that they stand for [46], it might still be worthwhile to expand the cluster to include more than one LiBH<sub>4</sub> unit. Of course, this will significantly raise the complexity of the investigation, but could be the only way to identify overlooked mechanisms in which a cooperative interaction between several LiBH<sub>4</sub> units on the surface of a C<sub>60</sub> leads to a reduction in hydrogen removal energy. Certainly, there are many more questions to be answered before we have a complete understanding of the catalysing effects of carbon nanomaterials on complex light metal hydrides, and we hope that the present work has not merely contributed some new insights to this field, but, perhaps more importantly, will also stimulate fresh theoretical and experimental investigations.

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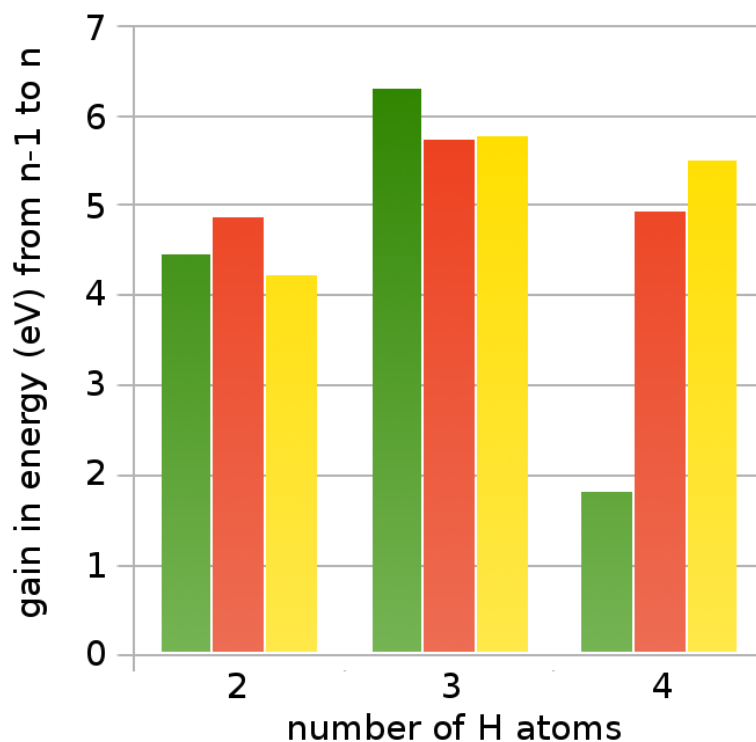
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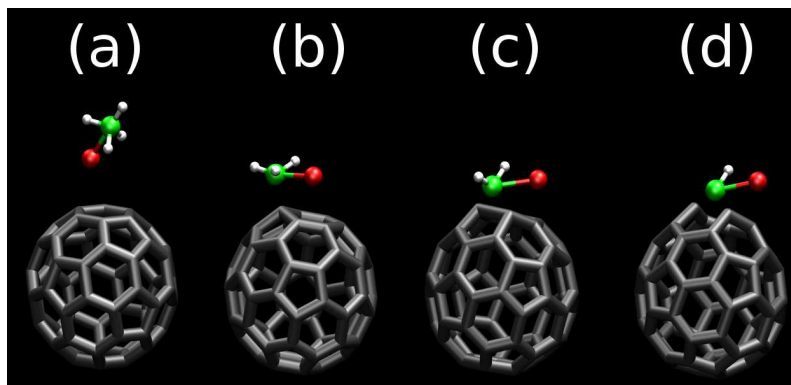
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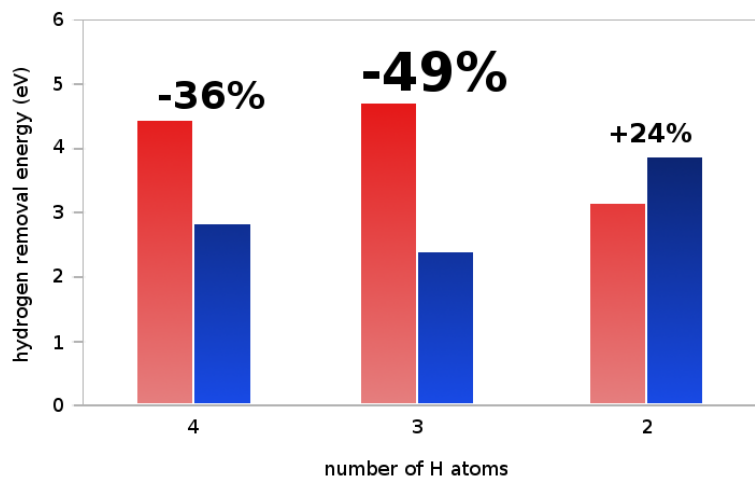




**Figure 1.** This plot shows the energy gain when adding a hydrogen atom to the respective clusters of  $BH_{n-1}$  (left-side green bars),  $BH_{n-1}^-$  (central red bars), and  $LiBH_{n-1}$  (right-side yellow bars).



**Figure 2.** Step-wise dehydrogenation of  $LiBH_4$  catalysed by  $C_{60}$ . Shown here are the atomic configurations as obtained from *ab initio* geometry optimizations for fullerene plus (a)  $LiBH_4$ , (b)  $LiBH_3$ , (c)  $LiBH_2$ , and (d)  $LiBH$ . Li is colored in red, B in green, H in white, and C in gray.



**Figure 3.** The hydrogen removal energies are plotted as a function of hydrogen content in  $LiBH_x$  (from left to right for  $x = 4, 3$ , and  $2$  H atoms), in the absence of fullerene (left-side red bars) and when fullerene is present (right-side blue bars). The relative change in hydrogen removal energy due to presence of the  $C_{60}$  catalyst is printed above the bars.